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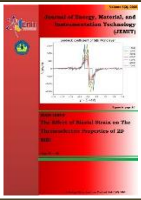

Manufacture of Nanocellulose from Red Onion Peel Waste Using Acid Hydrolysis Method with Variation of H_2SO_4 Concentration

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Abstract

This study investigates the effect of varying sulfuric acid (H_2SO_4) concentrations on the crystallite size and surface morphology of nanocellulose isolated from onion peel waste (Allium cepa). The nanocellulose production process consisted of three main stages: delignification using 10% sodium hydroxide (NaOH) to remove lignin and hemicellulose, bleaching with 10% hydrogen peroxide (H_2O_2) to eliminate residual impurities, and acid hydrolysis using H_2SO_4 at concentrations of 5%, 10%, 15%, and 20%. Characterization was conducted using X-ray Diffraction (XRD) to determine crystallite size and Scanning Electron Microscopy (SEM) to observe surface morphology. XRD results revealed that a 20% concentration of H_2SO_4 yielded the highest crystallinity, as indicated by the most prominent diffraction peak. SEM analysis showed that the resulting nanocellulose fibers tended to aggregate, forming bundles or agglomerates. These findings provide valuable insights for optimizing acid concentration in producing nanocellulose from lignocellulosic waste.

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Abstrak

Penelitian ini bertujuan untuk mengkaji pengaruh variasi konsentrasi asam sulfat (H_2SO_4) terhadap ukuran kristalit dan morfologi permukaan nanoselulosa yang diisolasi dari limbah kulit bawang merah. Nanoselulosa diproduksi melalui tiga tahap utama, yaitu delignifikasi menggunakan larutan natrium hidroksida (NaOH) 10% untuk menghilangkan lignin dan hemiselulosa, pemutihan menggunakan hidrogen peroksida (H_2O_2) 10% untuk menghilangkan sisa senyawa pengotor, serta hidrolisis asam menggunakan H_2SO_4 dengan variasi konsentrasi 5%, 10%, 15%, dan 20%. Karakterisasi dilakukan menggunakan *X-ray Diffraction* (XRD) untuk menentukan ukuran kristalit dan *Scanning Electron Microscopy* (SEM) untuk mengamati morfologi permukaan. Hasil XRD menunjukkan bahwa konsentrasi H_2SO_4 sebesar 20% menghasilkan ukuran kristalit tertinggi, yang menunjukkan tingkat kristalinitas terbaik. Sementara itu, hasil SEM memperlihatkan bahwa nanoselulosa yang diperoleh masih cenderung membentuk ikatan antar serat atau aglomerat. Temuan ini memberikan informasi penting mengenai optimasi konsentrasi asam dalam produksi nanoselulosa dari limbah lignoselulosa.

1. Introduction

Nanocellulose is a new type of material, and it is a cellulose extract that is processed into nano-size. Nanocellulose exploration has become of great interest in the last decade. Its advantages include good mechanical properties, low density, environmentally friendly, abundant raw materials, inexpensive, non-toxic, easily degraded, and included in renewable natural resources. Based on Inc Future Market (2012), the market share of nanocellulose in 2017 is estimated at US$ 97 million in biomedical and life sciences.

The continuous use of forest plants to produce cellulose fibers can reduce the area and amount of forest resources in Indonesia, which can cause forest damage, soil erosion, floods, landslides, and global warming. To reduce the negative impact caused by the cellulose production of these plants, it is necessary to find other alternatives to produce cellulose fiber. Cellulose fibers can be produced from plants, marine animals, and bacteria. Natural fiber from plants has many benefits and can be used as a source of nanocellulose, such as onion peel.

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Onion peel is part of the plant as a natural source of cellulose. Onion peel is a dry waste containing cellulose 41%-50%, hemicellulose 16-26%, and lignin 26-39% (Reddy & Rhim, 2018). More than half a million tonnes of onion waste are disposed of in the European Union every year (Benitez et al., 2011), and tonnes of onion waste are generated annually in Asian countries, one of which is in Japan more than 144,000 tonnes of onion waste are produced every year (Salak et al., 2013). Converting onion peel waste into nanocellulose material can be one solution to reduce onion peel waste that has not been utilized.

Several techniques have been developed to extract nanocellulose from cellulose, including chemical treatment (oxidation and acid hydrolysis), biological treatment (enzymatic hydrolysis), and mechanical processes. Each extraction method makes it possible to produce different types and properties of nanocellulose. Acid hydrolysis treatment is the most widely used process. It requires a faster reaction time than other processes, and acid hydrolysis treatment was chosen because it is a very efficient method and requires economical costs (Lee et al., 2014). Sulfuric acid is a type of acid that is widely used in the hydrolysis of cellulose. Strong acids can remove the amorphous part of the cellulose chain to be isolated on the crystalline part of cellulose (Klemm et al., 1998). The strong acids used in acid hydrolysis are particularly suitable for synthesizing nanocellulose. However, strong acids also have negative impacts, which are toxic, hawed, and corrosive, and the resulting waste is harmful to the environment (Ningtyas et al., 2020).

Previous research has been carried out by Hertiwi et al. (2020), who made nanocellulose from onion peel using sulfuric acid with a concentration of 50%. The study used variations in stirring time for the independent variable and the resulting nanocellulose size of 12.6 nm. Ieolovich (2012) made nanocellulose with variations in reaction temperature and the ratio of acid to cellulose, obtaining nanocellulose with a size of 10–20 nm. Ningtyas et al. (2020) made nanocellulose with variations in sulfuric acid concentrations of 45, 55 and 65% produced nanocellulose ranging from 356.5 - 764.2 nm from rice straw waste, while for the size of corn husk waste, nanocellulose ranged from 422.6 - 634 nm.

Characterization of nanocellulose is essential because the change of cellulose into nano-sized causes changes in the properties of cellulose. Cellulose changes are surface area changes, increased crystallinity and dispersion, and biodegradability. The biodegradation properties of nanocellulose can be used as a filler in bioplastic materials (Hertiwi. et al., 2020). The characterization of nanocellulose consists of four types, each serving a different function: Fourier Transform Infrared Reflectance (FTIR) analysis, X-ray diffraction (XRD) analysis, Scanning Electron Microscopy (SEM) analysis, and Transmission Electron Microscopy (TEM) analysis. FTIR analysis is conducted to observe the functional groups of nanocellulose (Skoog, 1998).

Based on the description above, this research will make nanocellulose from onion peel using a chemical method, namely acid hydrolysis, with a characterization test using XRD and SEM analysis. The acid used is sulfuric acid (H_2SO_4) with a low concentration variation of 5, 10, 15 and 20%. This low-concentration variation will determine the optimum concentration in manufacturing nanocellulose from onion peel waste and kepok banana peel waste.

2. Research Methods

The tools used in this study were beakers, measuring cups, Petri dishes, an Erlenmeyer flask, a hot plate, a magnetic stirrer, a water bath, an analytical balance, an oven, mortar, a spoon, a filter, and litmus paper. The materials used in this study were onion peel, NaOH, H_20_2, H_2SO_4, ethanol, and water deionized. The procedures carried out in this study included sample preparation, isolation of cellulose, synthesis of nanocellulose, and characterization of nanocellulose.

2.1 Sample Preparation

The first step in drying the onion peel is to dry it in the sun, then puree it using a blender until it becomes powder. After that, the smooth onion peel is washed with a 1:1 solution of distilled water and ethanol.

2.2 Cellulose Insulation

Onion peels as much as 5 grams per sample. Then, it was soaked with 50 ml of 10% NaOH solution, stirred using a magnetic stirrer, soaked for 24 hours, and filtered using a filter. The samples obtained were then soaked again with 50 ml of 10% H_20_2 solution for 24 hours. Then, the mixture was filtered, and the resulting sample was washed with distilled water to a neutral pH (7 times washing). After that, the samples were put in an oven with a temperature of 60℃ and dried.

2.3 Nanocellulose Insulation

This research uses a chemical method, acid hydrolysis, to synthesize nanocellulose. The onion peel samples will be divided into four samples with different concentrations of H_2SO_4, as shown in **Table 1**.

Table 1. Variation of research sample to be used

	Sample Name	Concentration
Onion Peel	A	5%
	B	10%
	C	15%
	D	20%

Onion peel was given 50 ml of H_2S0_4 solution with various concentrations of 5, 10, 15, and 20% and then heated with a water bath for 3.5 hours at a temperature of 50℃. After that, the mixture was filtered, and the resulting sample was washed and neutralized using distilled water. Then, the sample is placed in an oven at 60℃ to dry. Before being characterized, the sample was pulverized using a mortar.

2.4 Nanocellulose Insulation

The samples were characterized using XRD analysis to determine the crystallite size and crystallinity index of nanocellulose and SEM analysis to determine the morphology of nanocellulose. The size of the nanocellulose crystallite was calculated using the Scherrer equation, which is shown in **Equation 1** (Scherrer, 1918).

$$D = \frac{\kappa\lambda}{B\cos\theta} \quad (1)$$

where D is the size of the crystallite, κ is the form factor of the crystallite, λ is the wavelength of the X-ray, B is FWHM (Full Width at Half Maximum), and θ is the diffraction angle (Scherrer, 1918).

The crystallinity index was calculated using the Segal equation shown in **Equation 2** (Segal, 1959).

$$Crl = \frac{I_{002} - I_{am}}{I_{002}} \times 100\% \quad (2)$$

where Crl is the value of the crystallinity index, I_{002} is the crystallinity scattering intensity, and I_{am} is the amorphous scattering intensity (Segal, 1959).

3. Results and Discussions

3.1 Qualitative Analysis

XRD characterization was carried out to determine the crystallinity of nanocellulose produced from sulfuric acid hydrolysis. Figure 1 shows the results of XRD nanocellulose from onion peel waste with variations in H_2SO_4 concentrations.

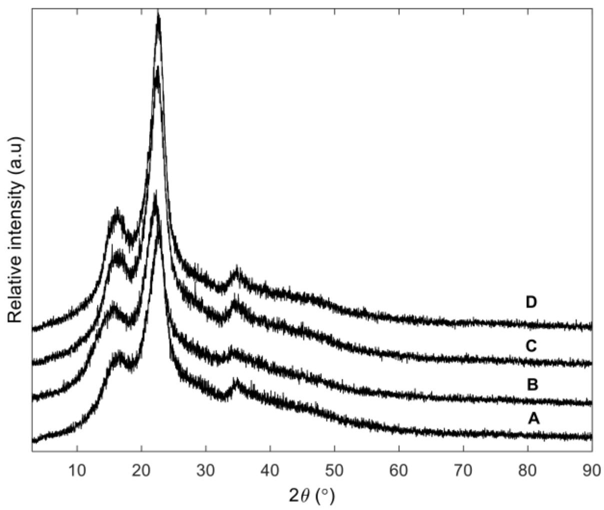

Figure 1. XRD results of onion peel nanocellulose

Figure 1 shows an illustration in the form of an XRD diffractogram of onion peel where there are three peaks in each sample. The highest peak at 2θ in each sample is the crystalline phase caused by the interaction between the hydroxyl group bonds in the cellulose to form a crystalline structure called the maximum crystal intensity (I_{002}). I_{002} produced onion peel nanocellulose at 2θ with concentrations of H_2SO_4 5, 10, 15, and 20%, respectively, at 22.3°, 22.5°, 22.6° and 22.8°. It shows the suitability of the diffraction numbers from the research of Yu et al. (2013). According to Yu, the diffraction pattern for the nanocellulose crystal plane has the highest peak intensity (I_{002}) at 2θ = 22°–23°. Its files are also reinforced by previous research conducted by Hertiwi et al. (2020), with a peak at 2θ, which is 22.6°.

Based on **Equation 1** and **Equation 2**, Table 2 shows the crystallite size results, and **Table** 3 shows the crystallinity index.

Table 2. Size of the onion peel nanocellulose crystallites with various acid concentrations

Sample	K	λ	B	θ	Crystallite size (nm)
A	0.94	0.154	5.0	11.15	3.4
B	0.94	0.154	4.3	11.25	3.9
C	0.94	0.154	4.1	11.30	4.1
D	0.94	0.154	3.6	11.40	4.7

Based on **Table 2**, the size of the nanocellulose crystallites ranged from 3.4 to 4.7 nm. According to Klemm (1998), this size shows appropriateness, which states that the nanocrystal size is usually in the range of 2-20 nm. Previous research conducted by Hertiwi et al. (2020) has made nanocellulose from onion peel with a concentration of 50% H_2SO_4, and the resulting nanocellulose crystallite size is 12.6 nm and in the research of Arjuna et al. (2018), which has made nanocellulose from cabbage waste fibers. With a concentration of H_2SO_4 65%, the resulting nanocellulose crystallite size is 58.91 nm. Compared with previous studies, the crystallite size differences are very much different. This could be due to the large concentration of H_2SO_4 used or the time spent in the acid hydrolysis process.

Table 3. Size of the onion peel nanocellulose crystallites with various acid concentrations

Sample	I_{002}	I_{am}	Crystallite index (%)
A	826	523	35.6
B	840.7	382.7	54.5
C	1209	455	62.4
D	1248	447	64.2

Based on **Table 3**, the nanocellulose crystallinity index ranged from 35.6 to 64.2%. The index shows the suitability of the numbers according to Klemm (1998), which states that the nanocrystalline crystallinity index is around 54-88%. Previous research conducted by Hertiwi et al. (2020) produced a nanocellulose crystallinity index of 78.7%. It indicates that the crystallinity index of the onion peel nanocellulose produced in the previous study was higher. This could be due to the large concentration of H_2SO_4 used and the hydrolysis time. The high crystallinity obtained was due to the removal of hemicellulose and lignin in the amorphous region, leading to the arrangement of the cellulose molecules.

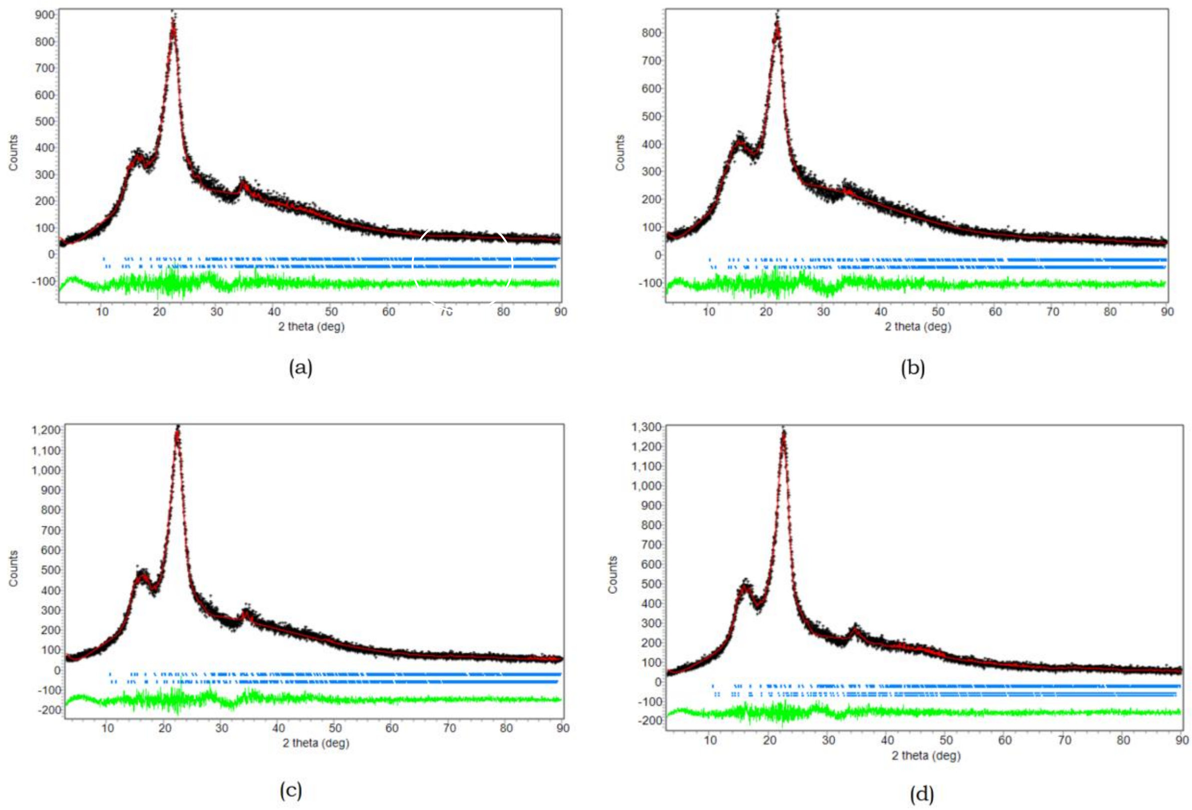

Figure 2. The results of refining XRD nanocellulose peel of onions with variations in concentration, a) 5% sample, b) 10% sample, c) 10% sample, and d) 20% sample

3.2 Quantitative Analysis

XRD data analysis using the Riestica application aims to quantitatively understand XRD data. The method used in Riestica is the Le Bail method. This method works by extracting intensity from diffraction data to obtain a suitable type of intensity so that it can be used to determine a crystal phase and refine information related to unit cells. The results of refining XRD data of onion peel nanocellulose with variations in H_2SO_4 concentrations are shown in **Figure 2**.

To apply the Le Bail method, it is necessary to estimate or possess data related to the lattice parameters of the phase. For onion peel nanocellulose, the lattice parameters used are $I\alpha$ and $I\beta$. In the XRD data refinement process, standard data is needed to fill in or compare the measured value with the standard value from Nishiyama et al. The phase $I\alpha$ value of the model refers to Nishiyama et al., 2003 and the phase $I\beta$ value of the model refers to Nishiyama et al., 2002. The phase $I\alpha$ CNC cell parameters are shown in **Table 3**, and the phase $I\beta$ CNC cell parameters are shown in **Table 4**.

Table 3. $I\alpha$ phase CNC cell parameters

Sample	a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)
Model	6.71	5.96	10.40	118.08	114.80	80.37
CNC 5%	6.73	6.03	10.64	118.74	115.88	79.35
CNC 10%	6.81	5.98	10.71	118.73	116.58	79.10
CNC 15%	6.78	6.05	10.66	118.27	116.49	78.89
CNC 20%	6.73	6.06	10.06	118.53	115.50	79.56

Table 4. $I\beta$ phase CNC cell parameters

Sample	a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)
Model	7.78	8.20	10.38	90.00	90.00	96.50
CNC 5%	7.83	8.28	10.54	90.00	90.00	96.83
CNC 10%	7.82	8.27	10.56	90.00	90.00	96.24
CNC 15%	7.83	8.30	10.54	90.00	90.00	96.87
CNC 20%	7.84	8.31	10.57	90.00	90.00	96.82

Based on **Table 2** and **Table 3**, the cell parameters of phase $I\alpha$ and $I\beta$ change compared to the standard values of Nishiyama et al. These changes can occur due to the effect of adding H_2SO_4 to the nanocellulose sample, and variations in the concentration of H_2SO_4 can affect the resulting crystallite size results.

SEM analyzed the morphology and dimensions of the crystal particles. The sample in the SEM was the best sample of onion peel nanocellulose, which was at a concentration of 20% H_2SO_4. The results of SEM nanocellulose from onion peel waste with a concentration of 20% H_2SO_4 are shown in **Figure 4**.

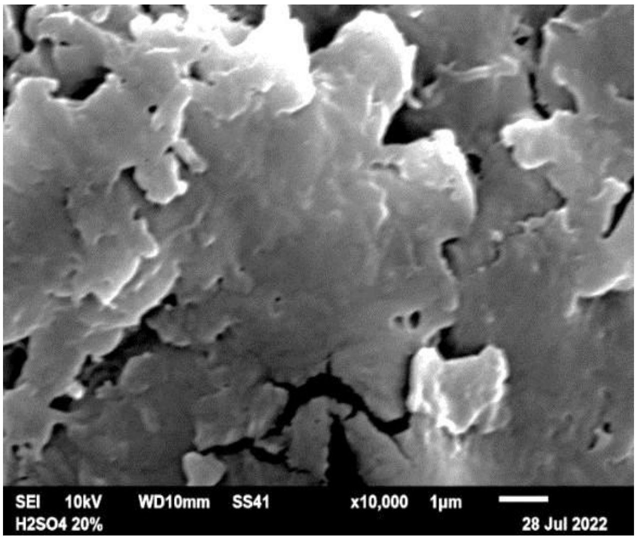

Figure 4. SEM results of onion peel nanocellulose

Figure 4 shows the morphology of onion peel nanocellulose at a scale of 1 m. It shows that not all cellulose fibers have become small cellulose fibrils because they are still united to form bundles or clumps. These results show similarities with previous studies conducted by Hertiwi et al. (2020). The level of crystal fineness strongly influences the incorporation of nanocellulose. Changes in the nanocellulose morphology cause the crystals' fineness to need to be considered to provide a small and better surface structure.

4. Conclusions

Based on the study's results, variations in the concentration of H_2SO_4 affect the size of the nanocellulose crystallites. The higher the concentration of H_2SO_4, the larger the size of the nanocellulose crystallites produced. The optimum concentration of H_2SO_4 to make nanocellulose from onion peel is 20%. Meanwhile, the onion peel nanocellulose morphology still unites to form rock plates.

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